

Claims

1. A process for the preparation of a grafted thermoplastic or elastomeric polymer or copolymer, which process comprises in a first step

A) the preparation of a nitroxyl terminated oligomer or polymer by controlled free radical polymerization of an ethylenically unsaturated monomer

a1) in the presence of a nitroxyl ether $R'R''N-O-X$ wherein X is selected such, that cleavage of the O-X bond occurs and a radical $X\bullet$ is formed capable of initiating polymerization; or

a2) in the presence of a nitroxyl radical $R'R''N-O\bullet$ and a free radical initiator capable of initiating polymerization; and in a second step

B) heating, mixing and reacting the nitroxyl terminated oligomer or polymer of step A) together with a thermoplastic or elastomeric polymer or copolymer at a temperature of between 120° C and 300° C.

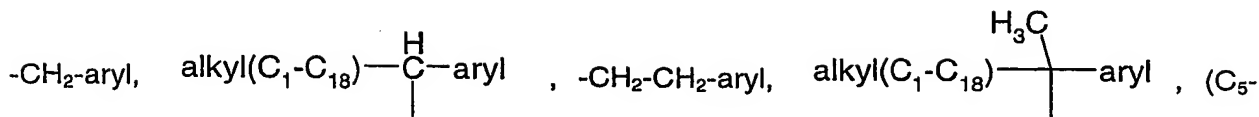
2. A process according to claim 1 wherein the thermoplastic or elastomeric polymer or copolymer is selected from the group consisting of a polyolefin and its copolymers, polystyrene and its block or graft copolymers, polymers and copolymers derived from 1,3-dienes.

3. A process according to claim 2 wherein the thermoplastic or elastomeric polymer or copolymer is selected from the group consisting of

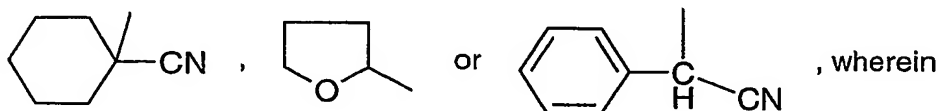
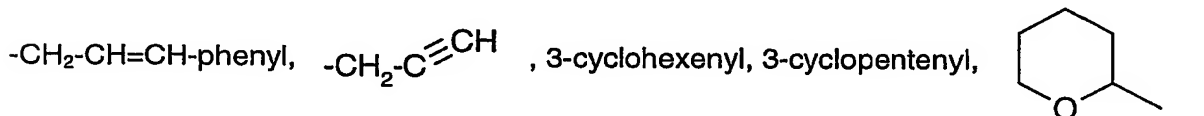
low density polyethylene (LDPE, LLDPE), high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), styrene-block copolymers (SI(S), SI, SB(S), ABS, ASA), ethylene-propylene-diene modified rubber (EPDM, EPM) and ethylene propylene rubber (EPR), polybutylene (PB), polyisobutylene (PIB), poly-4-methylpentene-1 (PMP).

4. A process according to claim 1 wherein the thermoplastic or elastomeric polymer or copolymer contains unsaturated bonds.

5. A process according to claim 1 wherein X is selected from the group consisting of



C₆cycloalkyl)₂CCN, (C₁-C₁₂alkyl)₂CCN, -CH₂CH=CH₂, (C₁-C₁₂)alkyl-CR₂₀-C(O)-(C₁-C₁₂)alkyl, (C₁-C₁₂)alkyl-CR₂₀-C(O)-(C₆-C₁₀)aryl, (C₁-C₁₂)alkyl-CR₂₀-C(O)-(C₁-C₁₂)alkoxy, (C₁-C₁₂)alkyl-CR₂₀-C(O)-phenoxy, (C₁-C₁₂)alkyl-CR₂₀-C(O)-N-di(C₁-C₁₂)alkyl, (C₁-C₁₂)alkyl-CR₂₀-CO-NH(C₁-C₁₂)alkyl, (C₁-C₁₂)alkyl-CR₂₀-CO-NH₂, -CH₂CH=CH-CH₃, -CH₂-C(CH₃)=CH₂,

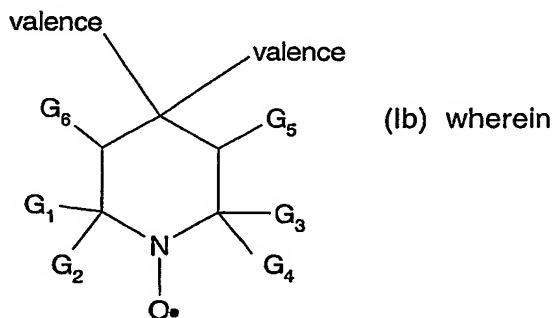
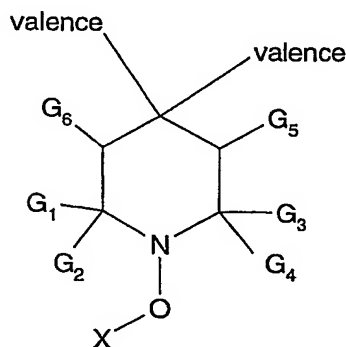


R₂₀ is hydrogen or C₁-C₁₂alkyl;

the alkyl groups are unsubstituted or substituted with one or more -OH, -COOH or -C(O)R₂₀ groups; and

the aryl groups are phenyl or naphthyl which are unsubstituted or substituted with C₁-C₁₂alkyl, halogen, C₁-C₁₂alkoxy, C₁-C₁₂alkylcarbonyl, glycidyloxy, OH, -COOH or -COO(C₁-C₁₂)alkyl.

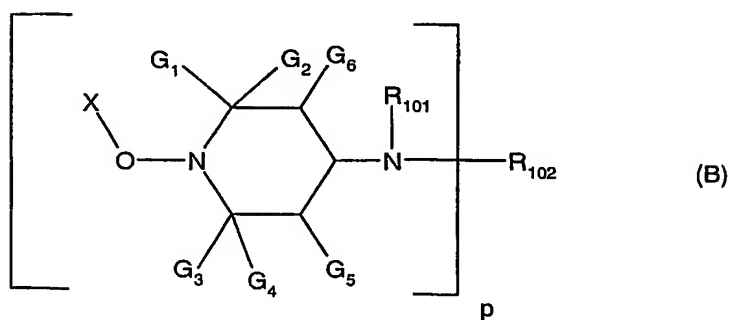
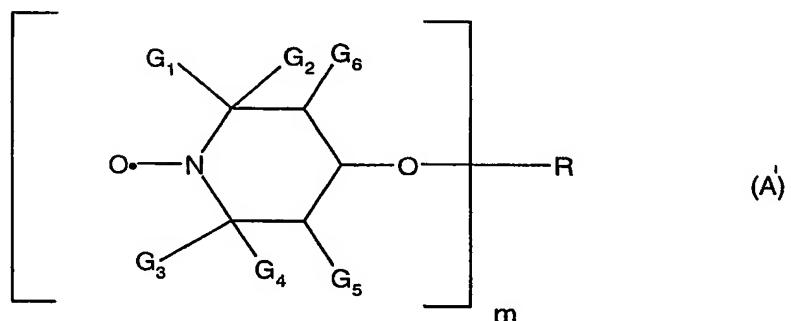
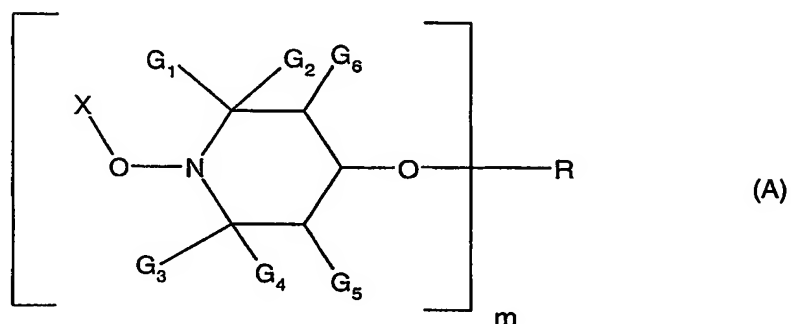
6. A process according to claim 1 wherein the nitroxyl-ether or the nitroxyl radical contains a structural element of formula (Ia) or (Ib)

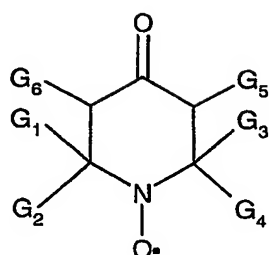
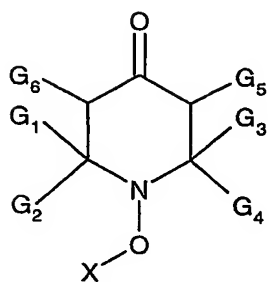
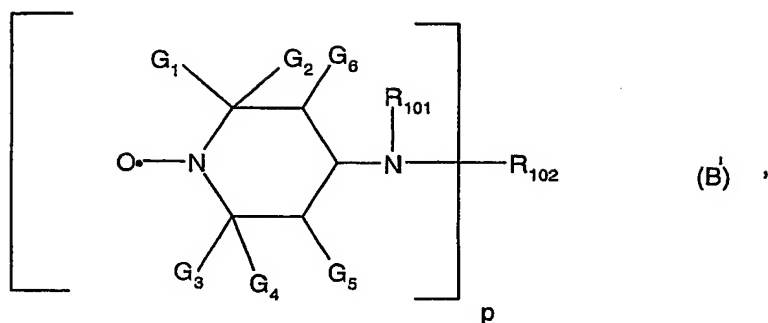


G₁, G₂, G₃, G₄ are independently C₁-C₆alkyl or G₁ and G₂ or G₃ and G₄, or G₁ and G₂ and G₃ and G₄ together form a C₅-C₁₂cycloalkyl group;

G_5 , G_6 independently are H, C_1 - C_{18} alkyl, phenyl, naphthyl or a group $COOC_1$ - C_{18} alkyl.

7. A process according to claim 6 wherein component a1) and a2) are of formula A, A', B, B' or O, O'





wherein

G₁, G₂, G₃ and G₄ are independently alkyl of 1 to 4 carbon atoms, or G₁ and G₂ together and G₃ and G₄ together, or G₁ and G₂ together or G₃ and G₄ together are pentamethylene;

G₅ and G₆ are independently hydrogen or C₁-C₄ alkyl;

m is 1, 2, 3 or 4

R, if m is 1, is hydrogen, C₁-C₁₈alkyl which is uninterrupted or C₂-C₁₈alkyl which is interrupted by one or more oxygen atoms, cyanoethyl, benzoyl, glycidyl, a monovalent radical of an aliphatic carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, or an α,β-unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms, where each carboxylic acid can be substituted in the aliphatic, cycloaliphatic or aromatic moiety by 1 to 3 -COOZ₁₂ groups, in which Z₁₂ is H, C₁-C₂₀alkyl, C₃-C₁₂alkenyl, C₅-C₇cycloalkyl, phenyl or benzyl; or R is a monovalent radical of a carbamic acid or phosphorus-containing acid or a monovalent silyl radical;

R, if m is 2, is C₂-C₁₂alkylene, C₄-C₁₂alkenylene, xylylene, a divalent radical of an aliphatic dicarboxylic acid having 2 to 36 carbon atoms, or a cycloaliphatic or aromatic dicarboxylic acid having 8-14 carbon atoms or of an aliphatic, cycloaliphatic or aromatic dicarbamic acid having 8-14 carbon atoms, where each dicarboxylic acid may be substituted in the aliphatic, cycloaliphatic or aromatic moiety by one or two -COOZ₁₂ groups; or

R is a divalent radical of a phosphorus-containing acid or a divalent silyl radical;

R, if m is 3, is a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid, which may be substituted in the aliphatic, cycloaliphatic or aromatic moiety by

-COOZ₁₂, of an aromatic tricarbamic acid or of a phosphorus-containing acid, or is a trivalent silyl radical,

R, if m is 4, is a tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid;

p is 1, 2 or 3,

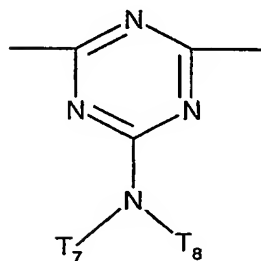
R₁ is C₁-C₁₂alkyl, C₅-C₇cycloalkyl, C₇-C₈aralkyl, C₂-C₁₈alkanoyl, C₃-C₅alkenoyl or benzoyl; when p is 1,

R₂ is C₁-C₁₈alkyl, C₅-C₇cycloalkyl, C₂-C₈alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula -CH₂CH(OH)-Z or of the formula -CO-Z- or -CONH-Z wherein Z is hydrogen, methyl or phenyl; or

when p is 2,

R₂ is C₂-C₁₂alkylene, C₆-C₁₂-arylene, xylylene, a -CH₂CH(OH)CH₂-O-B-O-CH₂CH(OH)CH₂-group, wherein B is C₂-C₁₀alkylene, C₆-C₁₅arylene or C₆-C₁₂cycloalkylene; or, provided that R₁ is not alkanoyl, alkenoyl or benzoyl, R₂ can also be a divalent acyl radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid, or can be the group -CO-; or R₁ and R₂ together when p is 1 can be the cyclic acyl radical of an aliphatic or aromatic 1,2- or 1,3-dicarboxylic acid; or

R₂ is a group



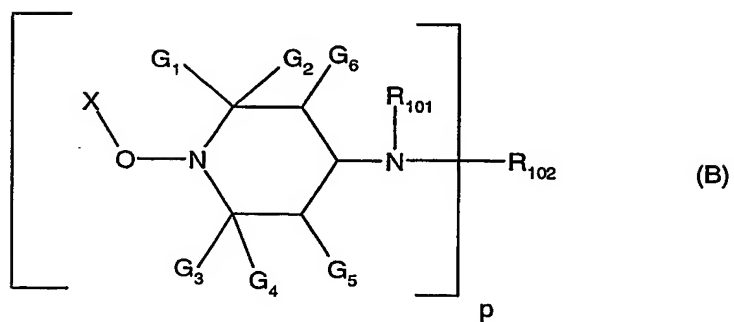
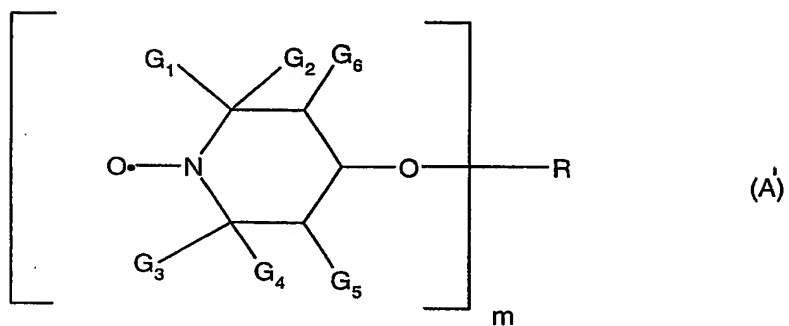
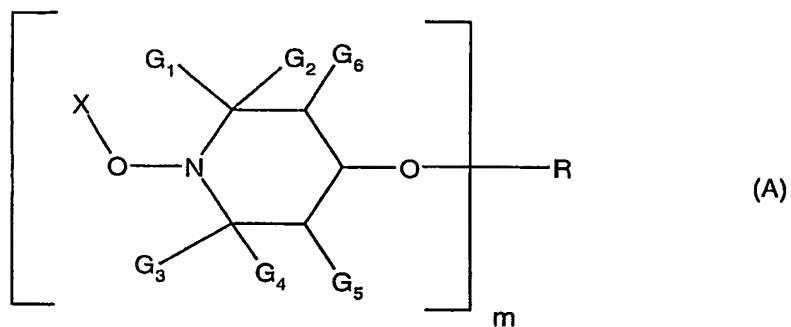
where T₇ and T₈ are independently hydrogen, alkyl of 1 to 18 carbon atoms, or T₇ and T₈ together are alkylene of 4 to 6 carbon atoms or 3-oxapentamethylene;

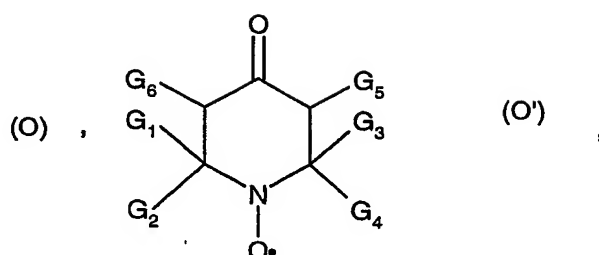
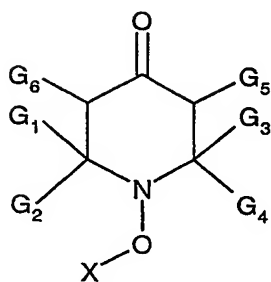
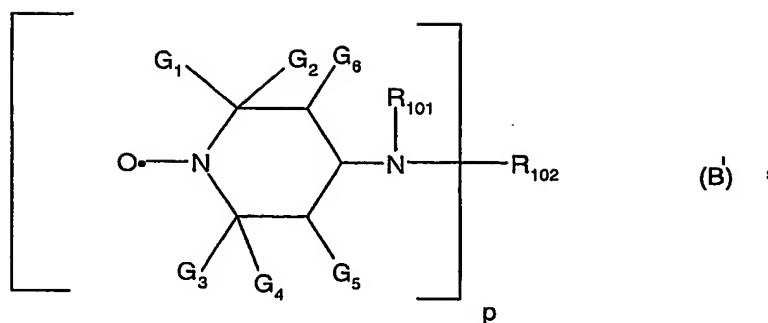
when p is 3,

R₂ is 2,4,6-triazinyl; and

X is as defined in claim 5.

8. A process according to claim 7 wherein component a1) and a2) are of formula A, A', B, B' or O, O'





wherein

m is 1,

R is hydrogen, C₁-C₁₈alkyl which is uninterrupted or interrupted by one or more oxygen atoms, cyanoethyl, benzoyl, glycidyl, a monovalent radical of an aliphatic carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, or an α,β -unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

p is 1;

R₁₀₁ is C₁-C₁₂alkyl, C₅-C₇cycloalkyl, C₇-C₈aralkyl, C₂-C₁₈alkanoyl, C₃-C₅alkenoyl or benzoyl;

R₁₀₂ is C₁-C₁₈alkyl, C₅-C₇cycloalkyl, C₂-C₈alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula -CH₂CH(OH)-Z or of the formula -CO-Z or -CONH-Z wherein Z is hydrogen, methyl or phenyl;

G₆ is hydrogen and G₅ is hydrogen or C₁-C₄alkyl,

G₁, G₂, G₃ and G₄ are methyl; or

G₁ and G₃ are methyl and G₂ and G₄ are ethyl or propyl or G₁ and G₂ are methyl and G₃ and G₄ are ethyl or propyl; and

X is selected from the group consisting of

-CH₂-phenyl, CH₃CH-phenyl, (CH₃)₂C-phenyl, (C₅-C₆cycloalkyl)₂CCN, (CH₃)₂CCN, -CH₂CH=CH₂, CH₃CH-CH=CH₂, (C₁-C₄alkyl)CR₂₀-C(O)-phenyl, (C₁-C₄)alkyl-CR₂₀-C(O)-(C₁-

C₄)alkoxy, (C₁-C₄)alkyl-CR₂₀-C(O)-(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-N-di(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-NH(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-NH₂, wherein R₂₀ is hydrogen or (C₁-C₄)alkyl.

9. A process according to claim 7 wherein G₂ and G₄ are ethyl, G₁ and G₃ are methyl, G₆ is hydrogen and G₅ is methyl.

10. A process according to claim 1 wherein the free radical initiator of component a2) is a bis-azo compound, a peroxide, a perester or a hydroperoxide.

11. A process according to claim 1, wherein the nitroxylether of component a1) or the nitroxyl radical of component a2) is present in an amount of from 0.001 mol-% to 20 mol-%, based on the monomer or monomer mixture.

12. A process according to claim 1, wherein the free radical initiator is present in an amount of from 0.001 mol-% to 20 mol-%, based on the monomer or monomer mixture.

13. A process according to claim 1, wherein the ethylenically unsaturated monomer is selected from the group consisting of styrene, substituted styrene, conjugated dienes, vinyl acetate, vinylpyrrolidone, vinylimidazole, maleic anhydride, (alkyl)acrylic acidanhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (meth)acrylonitriles, (alkyl)acrylamides, vinyl halides or vinylidene halides.

14. A process according to claim 12, wherein the ethylenically unsaturated monomer is a compound of formula CH₂=C(R_a)-(C=Z)-R_b, wherein R_a is hydrogen or C₁-C₄alkyl, R_b is NH₂, O⁻(Me⁺), glycidyl, unsubstituted C₁-C₁₈alkoxy, C₂-C₁₀₀alkoxy interrupted by at least one N and/or O atom, or hydroxy-substituted C₁-C₁₈alkoxy, unsubstituted C₁-C₁₈alkylamino, di(C₁-C₁₈alkyl)amino, hydroxy-substituted C₁-C₁₈alkylamino or hydroxy-substituted di(C₁-C₁₈alkyl)amino, -O-CH₂-CH₂-N(CH₃)₂ or -O-CH₂-CH₂-N⁺H(CH₃)₂ An⁻;

An⁻ is a anion of a monovalent organic or inorganic acid;

Me is a monovalent metal atom or the ammonium ion.

Z is oxygen or sulfur.

15. A process according to claim 1 wherein step B) is performed in an extruder, mixer or kneading apparatus.
16. A process according to claim 1 wherein in step B) additionally a processing stabilizer and/or antioxidant is added.
17. A process according to claim 1 wherein in step B) additionally a radical generator is added.
18. A process according to claim 1 wherein the nitroxyl terminated polymer or oligomer of step A) has an average molecular weight of from 1000 to 100 000 Dalton.
19. A process according to claim 1 wherein the nitroxyl terminated polymer or oligomer of step A) has a polydispersity PD from 1.0 to 2.0.
20. A process according to claim 1 wherein the nitroxyl terminated polymer or oligomer of step A) is added to the thermoplastic or elastomeric polymer or copolymer in an amount from 0.1% to 50% by weight based on the weight of the thermoplastic or elastomeric polymer or copolymer.
21. A grafted thermoplastic or elastomeric polymer or copolymer obtained according to claim 1.
22. Use of a nitroxyl terminated polymer or oligomer for the preparation of a grafted thermoplastic or elastomeric polymer or copolymer comprising heating mixing and reacting the nitroxyl terminated oligomer or polymer together with a thermoplastic or elastic polymer or copolymer at a temperature of between 120° C and 300° C.